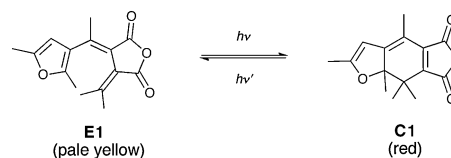


Photomechanical Motion of Furylfulgide Crystals

Hideko Koshima,* Hidemitsu Nakaya, Hidetaka Uchimoto, and Naoko Ojima
 Department of Materials Science and Biotechnology, Graduate School of Science and Engineering,
 Ehime University, Matsuyama, Ehime 790-8577

(Received September 28, 2011; CL-110798; E-mail: koshima.hideko.mk@ehime-u.ac.jp)

Plate-like microcrystals of a photochromic furylfulgide bend toward the light upon UV irradiation and then straighten upon visible light irradiation. The reversible bending was observed over 200 cycles of alternating irradiation with UV and visible light. The mechanism of bending could be explained by the X-ray crystallographic data.



Scheme 1. Photochromic reaction of furylfulgide **1**.

Creating mechanical motion in bulk materials based on geometric structural changes in individual molecules in response to external stimuli presents a scientific challenge. Artificial molecular mechanical systems, however, have not been linked to macroscale mechanical motion.¹ Large-scale mechanical motion of molecular materials has been reported only in liquid-crystal elastomers, in which a photoinduced order–disorder phase transition was used as the driving force.² Recently, mechanical bending of photochromic diarylethene crystals was reported, and the macroscale bending of the crystals was found to be caused by molecular-scale motion.³ Additionally, several photomechanical crystals composed of azobenzenes and salicylideneanilines have been reported to provide promising opportunities for artificial molecular machinery.^{4–9}

Fulgides constitute a class of photochromic compounds that undergo reversibly electrocyclic ring-closure and ring-opening reactions.¹⁰ The furylfulgide (*E*)-2-[1-(2,5-dimethyl-3-furyl)ethylidene]-3-isopropylidenesuccinic anhydride (**E1**) in *E*-form exhibits photochromism in the crystalline state (Scheme 1).^{11–13} This letter describes plate-like microcrystals of **E1** that reveal reversible bending upon alternate irradiation with UV and visible light. The bending mechanism is based on changes in crystal structure before and after photoirradiation.

Microcrystals of **E1** were prepared by sublimation of crystalline powders in a small platinum pan covered with a glass plate. Plate-like microcrystals grew on the surface of the glass plate after heating to approximately 20 °C below the melting point (126 °C) and holding for several hours (Figure S1). X-ray diffractograms of the microcrystals contained two peaks, which were assigned to the 101 and 202 reflections based on consistencies with existing crystallographic data (Figure S1¹⁵).^{11,13}

Figure 1a shows the hexagonal face of a plate-like **E1** microcrystal ($115 \times 60 \times 2 \mu\text{m}^3$) with the left end fixed to an adjacent crystal while the other portion is free. The top surface of the plate-like microcrystal was identified as the (101) face with its longitudinal direction along the *b* axis, based on comparisons with the bulk crystal having a hexagonal surface, which exhibits a (101) face along the *b* axis (Figure 1d). When the (101) face of the microcrystal was irradiated from the diagonal underside at 365 nm (10 mW cm^{-2}) with a UV-light-emitting diode (LED) for 1 s, the crystal curled from the right upper corner toward the light, reaching a maximum twisted curl

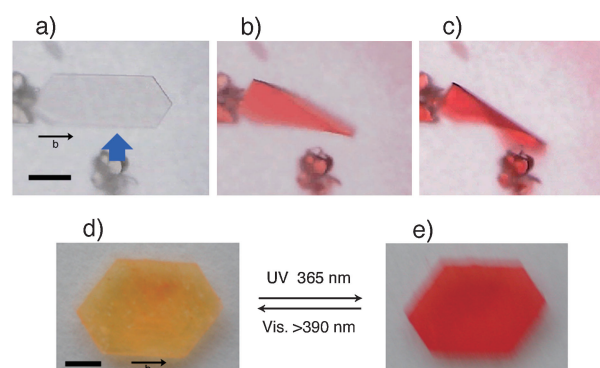


Figure 1. The (101) face of the plate-like **E1** microcrystal before (a) and after UV irradiation for (b) 1 and (c) 2 s. Scale bar: 50 μm . The (101) face of the bulk single crystal of **E1** before (d) and after UV irradiation (e). Scale bar: 1 mm.

after 2 s with a color change from pale yellow to red due to the formation of the closed **C1** isomer (Figures 1a–c and Video S1¹⁵). In contrast, a millimeter-scale bulk single crystal changed color upon UV irradiation, but the crystal shape did not change (Figures 1d and 1e).

When the (101) face of a narrow plate-like microcrystal ($109 \times 6 \times 2 \mu\text{m}^3$) was irradiated at 365 nm from the lower side, the crystal bent toward the light, reaching a maximum tip displacement angle of 9° after 2 s (Figures 2a and 2b, and Video S2¹⁵). Subsequent illumination with a halogen lamp equipped with a filter ($>390 \text{ nm}$, 10 mW cm^{-2}) returned the crystal to its initial straight shape after 30 s (Figure 2a). This reversible bending was observed over 200 cycles of alternating irradiation with UV (2 s) and visible light (30 s) (Figure 2c). The bending motion was accompanied by a color change from pale yellow to red ($\lambda_{\text{max}} = 512 \text{ nm}$) due to the formation of the closed **C1** isomer in the crystals (Figure S2¹⁵). The red crystal also returned to the initial pale yellow color due to the photochemical ring-opening reaction, generating the **E1** isomer.

The bending effect was ascribed to a gradient with respect to the extent of electrocyclic ring-closure as a function of light penetration, such that shrinkage of the irradiated crystal surface along the *b* axis resulted in a bent macrostructure. In the **E1** crystal, the **E1** molecules have torsional conformation with a

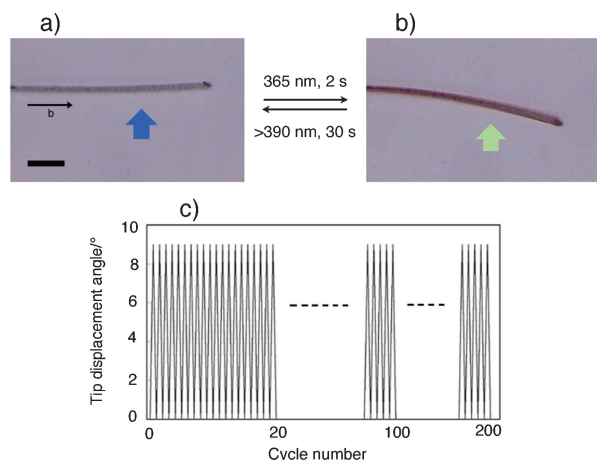


Figure 2. Bending of a narrow, plate-like crystal of **E1** (a) before and (b) after UV irradiation from the lower side. Scale bar: 20 μm . (c) Reversible bending was repeatable over as many as 200 cycles.

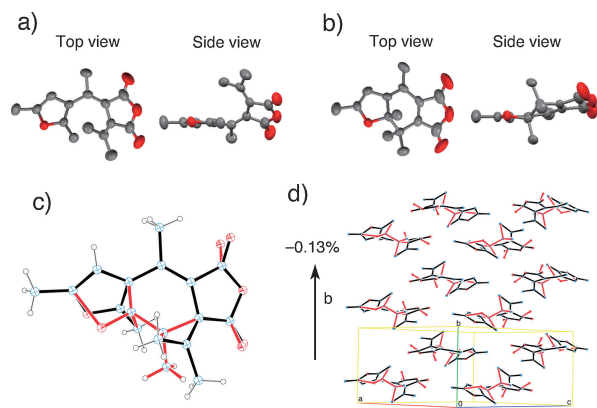


Figure 3. Molecular structures of (a) the **E1** isomer and (b) the **C1** isomer in the crystals of **E1** and **C1**, respectively. (c) ORTEP drawings show the disordered structures of the **E1** (black) and the **C1** (red) isomers after irradiation at 742 nm at the 25% probability level. (d) Molecular arrangement on the (101) face. Hydrogen atoms are omitted for clarity.

dihedral angle of 38.3° between the succinic anhydride portion and the furan ring (Figure 3a) and are arranged at the (101) face in a twofold screw along the b axis.¹¹ Upon UV irradiation, the torsional **E1** molecules underwent electrocyclic ring-closure to **C1** molecules on the (101) crystal surface. The crystalline **C1** isomer is nearly planar with a dihedral angle of 13.8° between the succinic anhydride portion and the furan rings (Figure 3b).¹³ Therefore, the ring-closure photoisomerization from the torsional **E1** isomer to the nearly planar **C1** isomer shrank the length of the b axis of the unit cell. By contrast, because photoisomerization does not occur in the absence of light, the unit cell dimensions remained constant for the nonilluminated surface, causing the microcrystals to bend toward the light source.

Crystallographic analysis of **E1** after two-photon excitation at 742 nm by pulsed laser light provides more direct evidence for the mechanism of photomechanical bending.¹⁴ The resulting crystal exhibited a disordered structure with contributions from

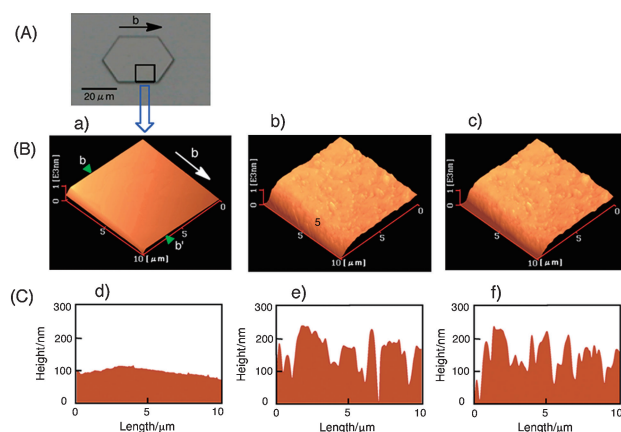


Figure 4. (A) Hexagonal (101) top face of an **E1** microcrystal, (B) atomic force microscopy images of the (101) surface and (C) the b - b' section before (a, d) and after irradiation with UV for 2 s (d, e) and then visible light for 20 min (c, f).

both the **E1** and the **C1** isomers at a ratio of 0.945:0.055 (Figure 3c). The length of the b axis of the unit cell decreased 0.13% from 9.6203(5) to 7.6101(8) \AA after two-photon excitation (Figure 3d), bending the plate-like microcrystal toward the light source.

The (101) top surface of the **E1** microcrystal was smooth before irradiation, as observed by atomic force microscopy (Figures 4a and 4d). After UV irradiation for 2 s, uneven features appeared with a height of 200 nm and a relative roughness of 18% of the crystal thickness (1100 nm) (Figures 4b and 4e). The relative intensity of X-ray diffraction peaks 101 and 202 of the microcrystals decreased to 63% and 50%, respectively, due to ring-closure photoisomerization to the **C1** isomer (Figure S1). Subsequent visible light irradiation for 20 min did not decrease the uneven features (Figures 4c and 4f). On the other hand, the diffraction peaks completely recovered their initial intensity due to ring-opening photoisomerization to the **E1** isomer (Figure S1), suggesting that the (101) smooth surface of the **E1** single crystal before irradiation changed to the **E1** polycrystalline state near the surface after irradiation with visible light. However, the correlation between the formation of the polycrystalline state and the bending behavior is not clear at the present time.

In conclusion, the photomechanical bending of plate-like microcrystals of the furylfulgide (*E*)-2-[1-(2,5-dimethyl-3-furyl)ethylidene]-3-isopropylidenesuccinic anhydride was repeated upon alternate irradiation with UV and visible light. The mechanism of bending could be explained by the X-ray crystallographic data.

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